

Future needs for NanoMetrology and Grand Challenges for the responsible commercialization of NanoTechnology.

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Nanotechnology is already here and has been for decades! DuPont has been manufacturing products with nanoscale architecture for a long time. We make polymers where the unique mechanical properties depend on 10 nanometer hard segments buried in a sea of liquid like polymer chains. Films only a few molecules thick protect fabrics, molded, and painted parts from stains and the environment. Catalysts used to create everything from environmentally friendly refrigerants to fertilizers rely on high surface area active metal particles. White pigments, sold literally by the ton, require ultra thin uniform coatings to protect the polymeric matrices from photo catalytic degradation. Ink jet inks utilize nano-sized pigments for a broad range of applications.

Recently there has been a dramatic improvement in our ability to measure, characterize, visualize and manipulate matter on scales that could only be imagined a decade ago. However, there are still significant challenges in metrology and characterization that if not overcome will hamper our ability to discover and commercialize new nanostructured materials, nanoparticles and nanocomposites with novel end use properties. While we are interested in a wide array of nanoscale science and engineering technologies the challenges articulated below address specifically our interest in nanoparticulate systems (composites, films, dispersions, etc.).

Grand Challenges and Hard Problems:

I. Determine coverage, thickness, and uniformity of thin coatings on nanoparticles.

Nanoparticles are almost always coated with something. In their natural state there is so much surface area, so many unsatisfied surface states that unless we do something to stop it they will agglomerate to reduce the overall surface free energy. Coatings can be organic dispersants or surfactants, or thin inorganic coatings. In the final article the surface coating can provide reactive sites to tie the nanoparticle into the polymer matrix to improve mechanical or other properties. Failure to engineer this surface appropriately can actually weaken the material instead of toughening it.

Developing and applying the functional coatings is difficult enough but determining the coverage and perfection of nanometer thick surface coatings on nanoparticles presents a significant challenge. In the ultimate case these coatings may be single monolayers surrounding and stabilizing particles that are as small as a few nanometers. (e.g. DNA wrapped single walled carbon nanotubes).

It is unlikely that a single technique will solve this problem. Any technique with sufficient resolution to analyze a single particle will need particular scrutiny to avoid statistical pitfalls. Global or macro techniques may miss important nanostructural features.

II. Determining the surface chemistry of nanoparticles on the nanoscale.

In most cases the maximum benefit of nanomaterials will rely on their successful incorporation into functional structures. Self-assembly of hierarchical structures, via for example chemical templates or DNA directed assembly, is expected to be a valuable part

of the manufacturing processes. These schemes involve the attachment of certain molecules to the nanoparticle through chemical bonding, and the surface chemistry of the particle plays a significant role. Present measurement techniques tend to see only the average or distribution of surface properties, not the individual active sites. When the interface of interest is buried or hidden within a matrix the problem becomes even more difficult. A high resolution means of quantifying the surface chemistry of nanoparticles is needed so that specific molecules can be attached in order to improve functionality or to construct (or control the assembly of) 3-D structures.

III. Statistical evaluation of dispersion of nanoparticles from synthesis through manufacturing and into the final consumer product.

As a result of the natural tendency for nanoparticles to agglomerate to reduce their overall surface area, complete dispersion during all phases of manufacturing and especially in the final nanocomposite material is of critical importance. If particles do agglomerate during one phase of the synthesis or manufacturing process, it is extremely challenging to get them to re-disperse.

Techniques exist to evaluate particle size and distribution in solutions and in free flowing powders, but the quality of the data depends on our ability to ensure complete disaggregation. When the particles are compounded into a solid matrix it is much more difficult to get a reliable, statistically significant measure of the dispersion. There are also challenges in measuring particle size distribution as the particles get smaller or when the particles are anisotropic in shape (nanotubes, nanorods, exfoliated clays). Of particular interest are methods to evaluate the length distribution of collections of anisotropic materials such as carbon nanotubes.

Commercialization may eventually require the development of surrogate measurement methods whenever possible to allow rapid assessment of nanocomposite properties and quality control. If all nanocharacterization has to be done on expensive research instruments the impact of nanotechnology on manufactured materials will be limited. Inexpensive, rapid, at-line or quality control instrumentation needs to be developed.

IV. Predicting macro/ bulk or end use properties based on nanoscale tests.

It is often difficult to predict the performance of a nanostructured material based on small-scale measurements. The end use application may be complex such as integration issues in a thin dielectric film or toughness and durability of a nanocomposite material. Instruments to evaluate the nanomechanical performance of polymers exist, but the connection of nanohardness, nanoscratch etc. to a particular end use is often difficult to establish. In those applications where the material will be used in thin film form or the mechanical damage is confined to the surface or near surface region existing nanomechanical tests can provide useful information about mechanical performance. However, even in such a case extracting intrinsic mechanical properties from the measurements is seldom straightforward.

V. Instrumentation or methods to sort or select nanoparticles based on size or properties

Successful commercialization of a nano-structured material may require the ability to select or sort the nanoparticles before use. For example, we may want only the semiconducting carbon nanotubes or a particular chirality or we may need to eliminate particles above a certain size because of a deleterious effect on mechanical or optical properties. Technology considered for this challenge will need to be robust, rapid, and suitable for incorporation into a manufacturing environment.

VI. Safety and Toxicology of Nanomaterials

There is a paucity of safety data on health risks related to exposures to nanoparticles. The major routes of potential occupational exposures to nanoscale materials are through the respiratory tract (inhalation), the skin, and the gastrointestinal tract (via oral or inhalation exposures). A method has been developed to evaluate the pulmonary hazards in experimental animals inhaling nanomaterials. Particle aggregation is a critical issue in influencing the deposition pattern and subsequent toxicity/biological activity of inhaled nanomaterials in the respiratory tract. Two of the major metrology-related challenges are precise particle size measurements while generating nanomaterial aerosols for inhalation toxicity studies (this is also a critical issue for exposure assessment studies at the workplace); and assessment of particle deposition patterns in the lungs of experimental animals following inhalation exposures – to determine whether aggregated nanoparticles have subsequently disaggregated into individual discrete nanoparticles following interactions with lung fluids at sites of particle deposition.

DuPont is committed to the safe and environmentally responsible introduction and commercialization of new Nanomaterials with novel properties and functionality that will benefit society. We are dedicated to understanding the impact of nanomaterials in both their benefits and any potential risks to safety, health and the environment. We advocate the generation of Safety, Health, and Environmental data on the materials of interest to us in an open, collaborative dialogue with other companies as well as other societal voices. It is core to DuPont to handle materials safely both in our hands and in the ultimate end products for which they are used. DuPont will support the development of standards, methods, and instrumentation to enable the safe development and use of Nanomaterials.



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